PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-045663

(43)Date of publication of application : 14.02.2003

(51)Int.Cl. H05B 33/22
C09K 11/06
H05B 33/14

(21)Application number : 2001-235058

(22)Date of filing : 02.08.2001

(71)Applicant : UNIV OSAKA

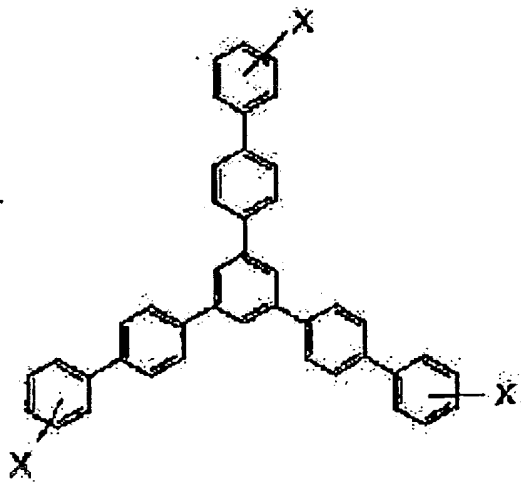
(72)Inventor : SHIROTA YASUHIKO
OKUMOTO KENJI

(54) MATERIAL FOR ELECTROLUMINESCENT ELEMENT, AMORPHOUS FILM, AND ELECTROLUMINESCENT ELEMENT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a new material for an electroluminescent element having a high blocking characteristic and being excellent in heat resistance and durability so that it is usable as a hole blocking layer in the electroluminescent element.

SOLUTION: The material for the electroluminescent element is represented by the general formula. In the formula, X represents either an electron withdrawing group or hydrogen and R represents either an alkyl group or hydrogen. The material for the electroluminescent element is formed into an amorphous film stable at or above room temperature, by heat melting and then standing to cool, or by vacuum deposition or the like. Because the amorphous film exhibits a high blocking characteristic due to the characteristic of the material, an electroluminescent element with a high emission efficiency can be obtained by using the amorphous film as a hole blocking layer.



LEGAL STATUS

[Date of request for examination] 02.08.2001

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	3671210
[Date of registration]	28.04.2005
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

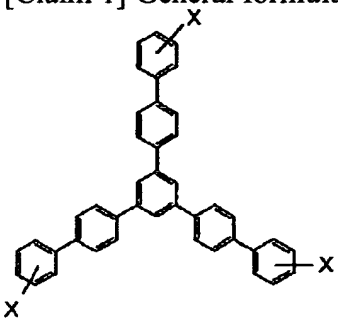
* NOTICES *

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

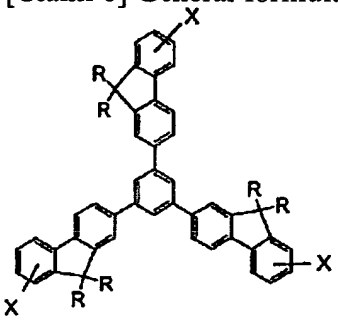
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] General formula [** 1]

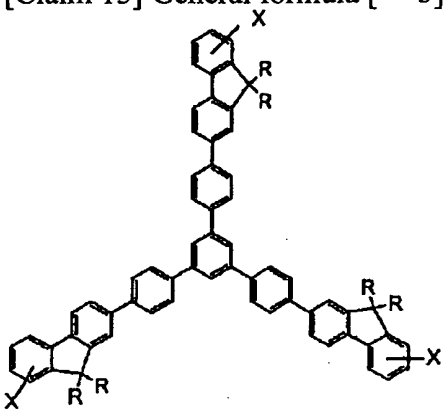


It is the charge of electroluminescent element material characterized by what is shown by (X expresses an electron withdrawing group or hydrogen among a formula).
[Claim 2] Said X is a charge of electroluminescent element material according to claim 1 characterized by being at least one of hydrogen, a halogen radical, a cyano group, and the nitro groups.
[Claim 3] 1, 3, and 5-Tori (biphenyl-4-IRU) -- benzene -- the charge of electroluminescent element material according to claim 2.
[Claim 4] 1, 3, and 5-tris (4'-fluoro biphenyl-4-IRU) -- benzene -- the charge of electroluminescent element material according to claim 2.
[Claim 5] 1, 3, and 5-tris (4'-cyano biphenyl-4-IRU) -- benzene -- the charge of electroluminescent element material according to claim 2.
[Claim 6] General formula [** 2]



It is the charge of electroluminescent element material characterized by what is shown by (X expresses an electron withdrawing group or hydrogen among a formula, and R expresses an alkyl group or hydrogen).
[Claim 7] Said X is a charge of electroluminescent element material according to claim 6 characterized by being at least one of hydrogen, a halogen radical, a cyano group, and the nitro groups.
[Claim 8] Said R is a charge of electroluminescent element material according to claim 6 or 7 characterized by being the alkyl group of carbon numbers 1-8.

[Claim 9] Said R is a charge of electroluminescent element material according to claim 8 characterized by being a methyl group.
[Claim 10] 1, 3, and 5-tris (9 and 9-dimethyl fluorene-2-IRU) -- benzene -- the charge of electroluminescent element material according to claim 9.
[Claim 11] 1, 3, and 5-tris (the 7-fluoro -9, 9-dimethyl fluorene-2-IRU) -- benzene -- the charge of electroluminescent element material according to claim 9.
[Claim 12] 1, 3, and 5-tris (7-cyano - 9 and 9-dimethyl fluorene-2-IRU) -- benzene -- the charge of electroluminescent element material according to claim 9.
[Claim 13] General formula [** 3]



It is the charge of electroluminescent element material characterized by what is shown by (X expresses an electron withdrawing group or hydrogen among a formula, and R expresses an alkyl group or hydrogen).
[Claim 14] Said X is a charge of electroluminescent element material according to claim 13 characterized by being at least one of hydrogen, a halogen radical, a cyano group, and the nitro groups.
[Claim 15] Said R is a charge of electroluminescent element material according to claim 13 or 14 characterized by being the alkyl group of carbon numbers 1-8.
[Claim 16] Said R is a charge of electroluminescent element material according to claim 15 characterized by being a methyl group.
[Claim 17] 1, 3, and 5-tris [4-(9 and 9-dimethyl fluorene-2-IRU) phenyl] -- benzene -- the charge of electroluminescent element material according to claim 16.
[Claim 18] 1, 3, and 5-tris [4-(7-fluoro -9, 9-dimethyl fluorene-2-IRU) phenyl] -- benzene -- the charge of electroluminescent element material according to claim 16.
[Claim 19] 1, 3, and 5-tris [4-(7-cyano - 9 and 9-dimethyl fluorene-2-IRU) phenyl] -- benzene -- the charge of electroluminescent element material according to claim 16.
[Claim 20] Amorphous film which consists of a charge of electroluminescent element material according to claim 1 to 19, and is characterized by presenting the shape of amorphous beyond a room temperature.
[Claim 21] The electroluminescent element characterized by having the electron hole blocking layer which consists of amorphous film according to claim 20.

[Translation done.]

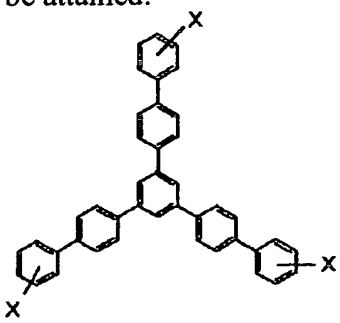
* NOTICES *

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

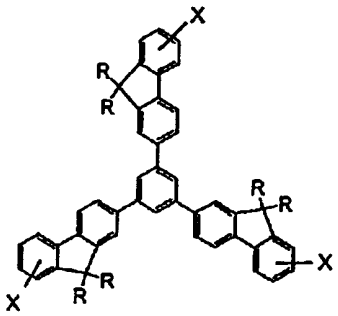
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the amorphous film which uses the charge of electroluminescent element material, and this ingredient, and an electroluminescent element.
[0002]
[Description of the Prior Art] In order to be utilization of an organic electroluminescent element (it may omit and may be hereafter called a "EL element"), it is required that efficient luminescence should be realized. For that purpose, it becomes important to balance the electron hole and electron which are poured into said EL element. In an EL element, the electron hole has become superfluous to the electron, and without recombining with an electron in a luminous layer, it will escape from said luminous layer and will usually come out of a superfluous electron hole. For this reason, although said luminous layer is made to usually adjoin and an electron hole blocking layer is prepared, development of an electron hole block ingredient has been an important technical problem that a high blocking property should be given to this electron hole blocking layer.
[0003] On the other hand, high thermal resistance and high endurance are required of the EL element itself from a viewpoint of application of an EL element. For example, about the application to a car-navigation system, the thermal resistance of 100 degrees C or more is called for. For this reason, naturally high thermal resistance and high endurance are required also about an electron hole blocking layer. Although some pi conjugated-system molecules were reported as the above-mentioned electron hole block ingredient until now, these were lacking in thermal resistance etc. and the blocking property itself was not still more enough for it.
[0004] This invention is excellent in thermal resistance and endurance, and aims at offering the new charge of electroluminescent element material which can be used as an electron hole blocking layer in an electroluminescent element and which has a high blocking property.
[0005]
[Means for Solving the Problem] This invention is a general formula [** 4] that the above-mentioned purpose should be attained.

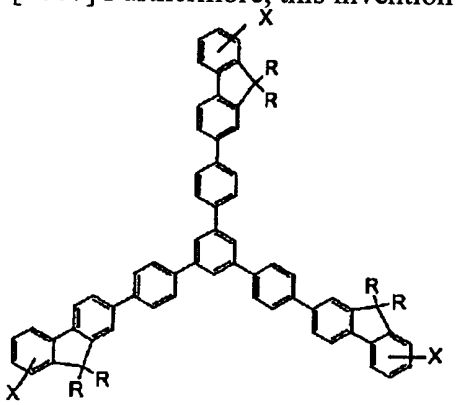


It is related with the charge of electroluminescent element material (1st charge of electroluminescent element material) characterized by what is shown by (X expresses an electron withdrawing group or hydrogen among a formula).
[0006] Moreover, this invention is a general formula [** 5].



It is related with the charge of electroluminescent element material (2nd charge of electroluminescent element material) characterized by what is shown by (X expresses an electron withdrawing group or hydrogen among a formula, and R expresses an alkyl group or hydrogen).

[0007] Furthermore, this invention is a general formula [** 6].



It is related with the charge of electroluminescent element material (3rd charge of electroluminescent element material) characterized by what is shown by (X expresses an electron withdrawing group or hydrogen among a formula, and R expresses an alkyl group or hydrogen).

[0008] this invention persons inquired wholeheartedly that the new charge of electroluminescent element material which can be used as an electron hole blocking layer of an EL element should be developed. Consequently, it found out that it could be made to make it amorphous easily by succeeding in composition of the new ingredient mentioned above, and forming this on a predetermined substrate or a substrate layer with a spin coat method or vacuum deposition.

[0009] And such amorphous film has a high glass transition temperature, holds an amorphous condition stably above a room temperature, and is excellent in thermal resistance and endurance. Furthermore, it has a high electron hole blocking property. Therefore, by constituting an electron hole blocking layer from said amorphous film, the omission of the electron hole out of a luminous layer can be controlled to altitude, and the EL element of high luminous efficiency can be obtained.

[0010] Hereafter, the concrete mode and concrete detail of this invention are explained to a detail based on the gestalt of implementation of invention.

[0011]

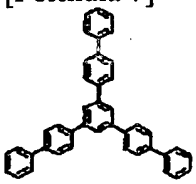
[Embodiment of the Invention] As for X in the chemical formula 4 of the 1st charge of electroluminescent element material mentioned above, it is desirable that it is at least one of a halogen radical, a cyano group, and the nitro groups, and it is especially desirable that it is at least one of hydrogen, a halogen radical, and the cyano groups. By this, an electron hole blocking property can be further raised in the thermal resistance of the 1st charge of electroluminescent element material and endurance, and a list. Moreover, any of the ortho position, the meta position, and the para position are sufficient as the location of X.

[0012] the case where X is specifically hydrogen -- 1, 3, and 5-Tori (biphenyl-4-IRU) -- benzene -- it is desirable to consist of compounds. The structure expression of this compound is expressed with a chemical formula 7. moreover,

the case where X is a halogen radical -- 1, 3, and 5-tris (4'-fluoro biphenyl-4-IRU) -- benzene -- it is desirable to consist of compounds. The structure expression of this compound is expressed with a chemical formula 8. furthermore, the case where X is a cyano group -- 1, 3, and 5-tris (4'-cyano biphenyl-4-IRU) -- benzene -- it is desirable to consist of compounds. The structure expression of this compound is expressed with a chemical formula 9.

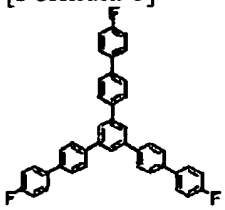
[0013]

[Formula 7]



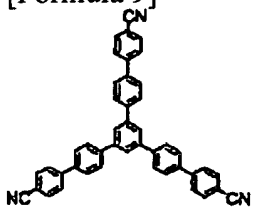
[0014]

[Formula 8]



[0015]

[Formula 9]



[0016] 1, 3, and 5-Tori (biphenyl-4-IRU) -- benzene -- a compound can be obtained by carrying out reflux churning and carrying out the Suzuki coupling reaction of 1, 3, and 5-tris (4-iodine phenyl) benzene and the phenyl boron acid in nitrogen-purge conditions, by making tetrakis (triphenyl phosphino palladium (0)) into a catalyst in the mixed solution of a tetrahydro furan and the potassium carbonate water solution of 2 conventions.

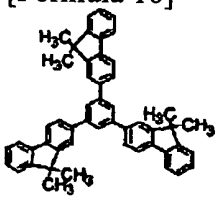
[0017] 1, 3, and 5-tris (4'-fluoro biphenyl-4-IRU) -- benzene -- a compound and 1 and 3, and 5-tris (4'-cyano biphenyl-4-IRU) -- benzene -- a compound can be replaced with the above-mentioned phenyl boron acid, and can be obtained by using 4-fluoro phenyl boron acid and 4-cyanophenyl boron acid, respectively.

[0018] As for X in the chemical formula 2 of the 2nd charge of electroluminescent element material mentioned above, it is desirable that it is at least one of a halogen radical, a cyano group, and the nitro groups like the above, and it is especially desirable that it is at least one of hydrogen, a halogen radical, and the cyano groups. Moreover, 5, 6, and any of the 7 or 8th place are sufficient as the location of X.

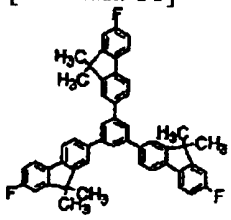
[0019] Moreover, as for R in a chemical formula 5, it is desirable that it is the alkyl group of carbon numbers 1-8, and it is desirable that it is a methyl group further. By this, an electron hole blocking property can be further raised in the thermal resistance of the 2nd charge of electroluminescent element material and endurance, and a list.

[0020] the case where X is specifically hydrogen -- 1, 3, and 5-tris (9 and 9-dimethyl fluorene-2-IRU) -- benzene -- it is desirable to consist of compounds. The structure expression of this compound is expressed with a chemical formula 10. moreover, the case where X is a halogen radical -- 1, 3, and 5-tris (the 7-fluoro -9, 9-dimethyl fluorene-2-IRU) -- benzene -- it is desirable to consist of compounds. The structure expression of this compound is expressed with a chemical formula 11. furthermore, the case where X is a cyano group -- 1, 3, and 5-tris (7-cyano - 9 and 9-dimethyl fluorene-2-IRU) -- benzene -- it is desirable to consist of compounds. The structure expression of this compound is expressed with a chemical formula 12.

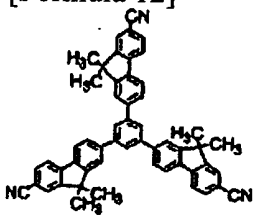
[0021]
[Formula 10]



[0022]
[Formula 11]

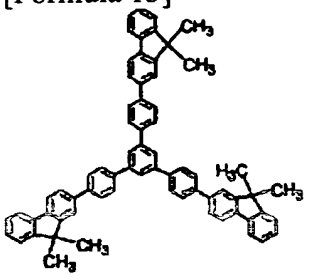


[0023]
[Formula 12]



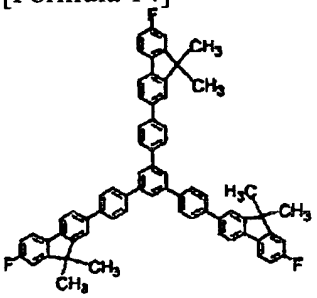
[0024] 1, 3, and 5-tris (9 and 9-dimethyl fluorene-2-IRU) -- benzene -- a compound For example, 1, 3, and 5-TORIBUROMO benzene and a 9 and 9-dimethyl fluorene-2-IRUBORON acid are set on nitrogen-purge conditions by making tetrakis (triphenyl phosphino palladium (0)) into a catalyst. It can obtain by carrying out reflux churning and carrying out the Suzuki coupling reaction in the mixed solution of a tetrahydro furan and the potassium carbonate water solution of 2 conventions.
[0025] moreover, 1, 3, and 5-tris (the 7-fluoro -9, 9-dimethyl fluorene-2-IRU) -- benzene -- a compound and 1 and 3, and 5-tris (7-cyano - 9 and 9-dimethyl fluorene-2-IRU) benzene -- benzene -- a compound It replaces with the above 9 and a 9-dimethyl fluorene-2-IRUBORON acid, and is 7-fluoro, respectively. - A 9 and 9-dimethyl fluorene-2-IRUBORON acid and 7-cyano - It can obtain by using a 9 and 9-dimethyl fluorene-2-IRUBORON acid.
[0026] As for X in the chemical formula 6 of the 3rd charge of electroluminescent element material mentioned above, it is desirable that it is at least one of a halogen radical, a cyano group, and the nitro groups like the above, and it is especially desirable that it is at least one of hydrogen, a halogen radical, and the cyano groups. Moreover, 5, 6, and any of the 7 or 8th place are sufficient as the location of X.
[0027] Moreover, as for R in a chemical formula 6, it is desirable that it is the alkyl group of carbon numbers 1-8, and it is desirable that it is a methyl group further. By this, an electron hole blocking property can be further raised in the thermal resistance of the 3rd charge of electroluminescent element material and endurance, and a list.
[0028] the case where X is specifically hydrogen -- 1, 3, and 5-tris [4-(9 and 9-dimethyl fluorene-2-IRU) phenyl] -- benzene -- it is desirable to consist of compounds. The structure expression of this compound is expressed with a chemical formula 13. moreover, the case where X is a halogen radical -- 1, 3, and 5-tris [4-(7-fluoro -9, 9-dimethyl fluorene-2-IRU) phenyl] -- benzene -- it is desirable to consist of compounds. The structure expression of this compound is expressed with a chemical formula 14. furthermore, the case where X is a cyano group -- 1, 3, and 5-tris [4-(7-cyano - 9 and 9-dimethyl fluorene-2-IRU) phenyl] -- benzene -- it is desirable to consist of compounds. The structure expression of this compound is expressed with chemistry 15.
[0029]

[Formula 13]



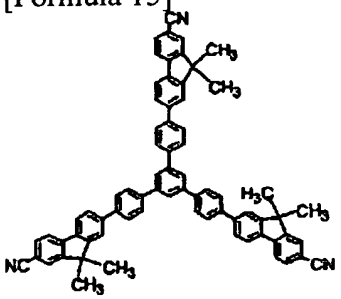
[0030]

[Formula 14]



[0031]

[Formula 15]



[0032] 1, 3, and 5-tris [4-(9 and 9-dimethyl fluorene-2-IRU) phenyl] -- benzene -- a compound For example, 1, 3, and 5-tris (4-iodine phenyl) benzene and a 9 and 9-dimethyl fluorene-2-IRUBORON acid are set on nitrogen-purge conditions by making tetrakis (triphenyl phosphino palladium (0)) into a catalyst. It can obtain by carrying out reflux churning and carrying out the Suzuki coupling reaction in the mixed solution of a tetrahydro furan and the potassium carbonate water solution of 2 conventions.

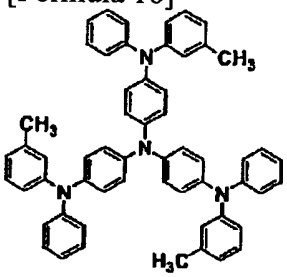
[0033] moreover, 1, 3, and 5-tris [4-(7-fluoro -9, 9-dimethyl fluorene-2-IRU) phenyl] -- benzene -- a compound and 1 and 3, and 5-tris [4-(7-cyano - 9 and 9-dimethyl fluorene-2-IRU) phenyl] benzene It replaces with the above 9 and a 9-dimethyl fluorene-2-IRUBORON acid, and is 7-fluoro, respectively. - A 9 and 9-dimethyl fluorene-2-IRUBORON acid and 7-cyano - It can obtain by using a 9 and 9-dimethyl fluorene-2-IRUBORON acid.

[0034] The charge of electroluminescent element material mentioned above can be formed as amorphous film by applying on a predetermined substrate or a substrate layer with the spin coat method from a solution cooled on both sides of the obtained melt which carried out heating fusion with two substrates (radiationnal cooling), or using the membrane formation technique, such as vacuum deposition.

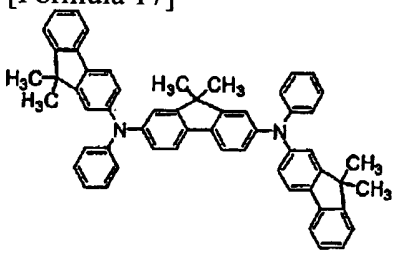
[0035] This amorphous film maintains an amorphous condition stably above a room temperature, and has high thermal resistance and high endurance. Moreover, a high blocking property can be shown and it can use suitably as an electron hole blocking layer of an electroluminescent element. Therefore, it is high thermal resistance and high endurance, and the electroluminescent element of high luminous efficiency can be obtained.

[0036]

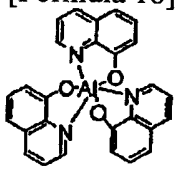
[Example] In this example, the luminous efficiency was evaluated by forming an electron hole blocking layer from the charge of electroluminescent element material of this invention, and producing an electroluminescent element.
[0037] (Production of an electroluminescent element) Drawing 1 is drawing showing the configuration of the electroluminescent element 10 produced in this example. The electroluminescent element 10 shown in drawing 1 is presenting the configuration to which the laminating of the ITO electrode 2, the electron hole transportation layer 3, a luminous layer 4, the electron hole blocking layer 5, the electronic transportation layer 6, and the back plate 7 was carried out one by one on the glass substrate 1.
[0038] an electron hole -- transportation -- a layer -- three -- (-- four -- four -- ' -- four -- ' -- ' - tris -- [-- three - methylphenyl (phenyl) -- amino --] -- a triphenylamine --) -- from -- a vacuum deposition method -- 500A in thickness -- forming -- a luminous layer 4 -- N, N, N', and N' - tetrakis (9 and 9-dimethyl fluorene-2-IRU)-[1 and 1'-biphenyl]-4 and 4' -- similarly it formed in 200A in thickness with the vacuum deposition method from - diamine. Moreover, for the electron hole blocking layer 5, it forms in 100A in thickness with a vacuum deposition method from 1 of this invention shown with chemical formula 10, 3, and 5-tris [4-(9 and 9-dimethyl fluorene-2-IRU) phenyl] benzene, and the electronic transportation layer 6 (from tris (8-quinolinolato) aluminum, it formed in 200A in thickness with the vacuum deposition method.) is, In addition, the back plate 7 was constituted from a MgAg electrode, and used the thing of 50 ohm/cm 2 as an ITO electrode 2.
[0039] moreover, a chemical formula 16 shows the general formula of the above (4, 4', and 4" - tris [3-methylphenyl (phenyl) amino] triphenylamine) -- having -- Above N and N, N', and N' - tetrakis (9 and 9-dimethyl fluorene-2-IRU)-[1 and 1'-biphenyl]-4 and 4' -- the structure expression of - diamine is shown by the chemical formula 17. Furthermore, the above (the structure expression of tris (8-quinolinolato) aluminum is shown by the chemical formula 18.)
[0040]
[Formula 16]



[0041]
[Formula 17]



[0042]
[Formula 18]



[0043] (Evaluation of an electroluminescent element) Drawing 2 is a graph which shows the emission spectrum of the electroluminescent element 10 produced as mentioned above. The emission spectrum shown in drawing 2 impresses

and obtains the electrical potential difference of 8V in a room temperature among atmospheric air between the ITO electrode 2 and the MgAg back plate 7. Luminescence of the dark blue from a luminous layer 4 was obtained from the electroluminescent element 10, and it was checked that each class containing the electron hole blocking layer 5 is functioning effectively so that clearly from drawing 2 .

[0044] Drawing 3 is a graph which shows the electrical-potential-difference-brightness property and voltage-current consistency property of an electroluminescent element 10. When the ITO electrode 2 side was made into forward potential, luminescence of dark blue was checked by impressing the electrical potential difference beyond 3V. Moreover, the highest brightness was 2240 cd/m2 in 13V, the luminous efficiency in 300 cd/m the light-hour of two shots was 0.20 lm/W, and quantum efficiency was 1.1%. That is, while the electroluminescent element 10 obtained in this example had high luminous efficiency, having luminescence brightness high enough was checked.

[0045] As mentioned above, although this invention has been explained to a detail based on the gestalt of implementation of invention, giving an example, unless it is not limited to the above-mentioned contents and deviates from the criteria of this invention, all deformation and modification are possible for this invention.

[0046]

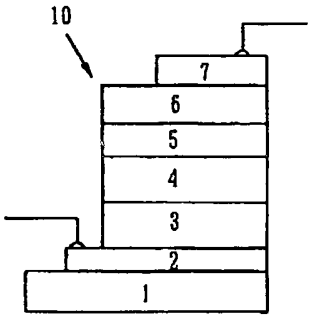
[Effect of the Invention] As explained above, according to the charge of electroluminescent element material of this invention, the amorphous film which was excellent in stable thermal resistance and endurance above the room temperature can be offered. This amorphous film originates in the property of said charge of electroluminescent element material, and shows a high electron hole blocking property. For this reason, by constituting an electron hole blocking layer from said amorphous film, the omission of the electron hole from a luminous layer can be controlled effectively, and the electroluminescent element excellent in luminous efficiency can be offered.

[0047] Moreover, it can originate in the high thermal resistance of said charge of electroluminescent element material, and high endurance, high thermal resistance and endurance can be given to said electroluminescent element, and it can be used for the car-navigation system in a severe environmental condition, for example, an automatic in the car one, etc.

[Translation done.]

THIS PAGE BLANK (USPTO)

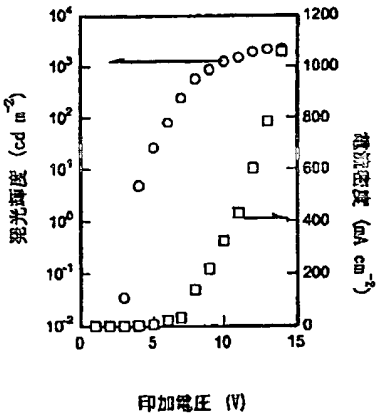
Drawing selection drawing 1



[Translation done.]

THIS PAGE BLANK (USPTO)

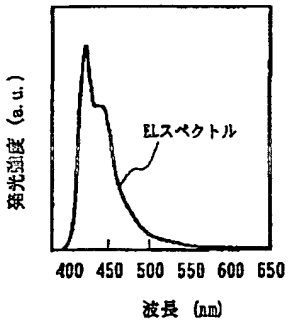
Drawing selection drawing 2



[Translation done.]

THIS PAGE BLANK (USPTO)

Drawing selection drawing 3



[Translation done.]

THIS PAGE BLANK (USPTO)